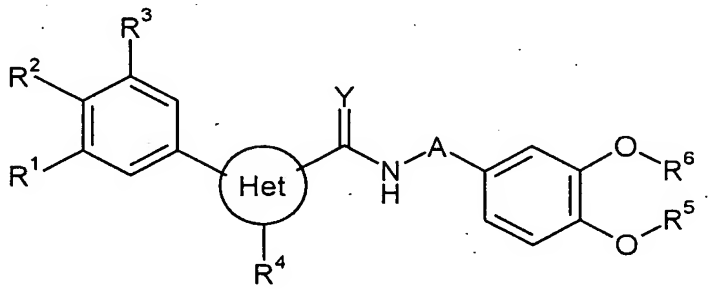
**Amides**

The invention relates to amides, to a plurality of processes for their preparation and to their use for controlling harmful organisms.

Amides having fungicidal properties are known, for example, from JP 2001348378. However, in some cases there is scope for improving the fungicidal action of these compounds.

However, since the ecological and economical demands made on modern fungicides are increasing constantly, for example with respect to activity spectrum, toxicity, selectivity, application rate, formation of residues and favorable manufacture, and there can furthermore be problems, for example, with resistance, there is a constant need to develop novel fungicides which, at least in some areas, have advantages over those of the prior art.

This invention provides novel compounds of the formula (I)




(I)

in which

$R^1$, $R^2$, and $R^3$ are identical or different and independently of one another represent hydrogen, halogen, cyano, nitro,

in each case straight-chain or branched alkyl, alkoxy, alkylthio, alkylsulfinyl or alkylsulfonyl having in each case 1 to 8 carbon atoms;

in each case straight-chain or branched alkenyl, alkynyl, alkenyloxy or alkynyloxy having in each case 2 to 6 carbon atoms;

in each case straight-chain or branched haloalkyl, haloalkoxy, haloalkylthio, haloalkylsulfinyl or haloalkylsulfonyl having in each case 1 to 6 carbon atoms and 1 to 13 identical or different halogen atoms;

in each case straight-chain or branched haloalkenyl or haloalkenyloxy having in each case 2 to 6 carbon atoms and 1 to 13 identical or different halogen atoms;

in each case straight-chain or branched alkylamino, dialkylamino, alkylcarbonyl, alkoxy-

carbonyl, hydroximinoalkyl or alkoximinoalkyl having in each case 1 to 6 carbon atoms in the individual alkyl moieties;

cycloalkyl having 3 to 6 carbon atoms,

where

$R^1$, $R^2$, and $R^3$ do not simultaneously represent hydrogen, or

$R^1$ and $R^2$ together with the carbon atoms to which they are attached form a carbocyclic ring,

Het represents an unsubstituted or substituted five-membered aromatic heterocyclic ring,

$R^4$ represents hydrogen, halogen, cyano, alkyl having 1 to 8 carbon atoms, alkenyl or alkynyl having 2 to 8 carbon atoms or haloalkyl having 1 to 8 carbon atoms and 1 to 9 halogen atoms,

$R^5$ and $R^6$ are identical or different and independently of one another represent unsubstituted or in each case halogen- or cyano-substituted alkyl, alkoxyalkyl having in each case 1-8 carbon atoms in the respective alkyl chains or alkenyl or alkynyl having in each case 2-8 carbon atoms or cycloalkyl having 3-8 carbon atoms or represent unsubstituted or substituted arylalkyl having 1-8 carbon atoms in the alkyl chain,

A represents alkanediyl or cycloalkanediyl and

Y represents oxygen or sulfur.

In the definitions, the saturated or unsaturated hydrocarbon chains, such as alkyl, alkanediyl, alkenyl or alkynyl, are in each case straight-chain or branched, including in combination with heteroatoms, such as in alkoxy, alkylthio or alkylamino.

Halogen generally represents fluorine, chlorine, bromine or iodine, preferably fluorine, chlorine or bromine, in particular fluorine or chlorine.

Aryl represents aromatic mono- or polycyclic hydrocarbon rings, such as, for example, phenyl, naphthyl, anthranyl, phenanthryl, preferably phenyl or naphthyl, in particular phenyl.

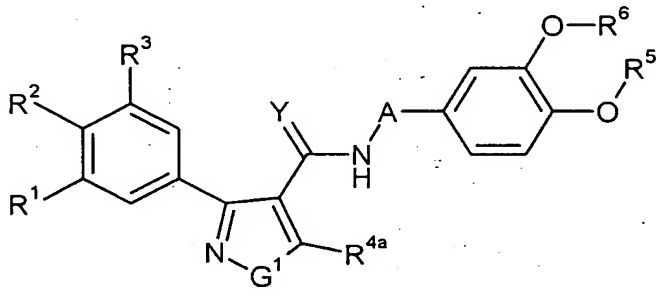
Cycloalkyl represents saturated carbocyclic cyclic compounds which, if appropriate, form, together with further carbocyclic fused-on or bridged rings, a polycyclic ring system.

Cycloalkenyl represents carbocyclic cyclic compounds which contain at least one double bond and which, if appropriate, form, together with further carbocyclic fused-on or bridged rings, a polycyclic ring system.

Furthermore, it has been found that the novel amides of the general formula (I) are highly active against harmful organisms and, in particular, have strong fungicidal action.

If appropriate, the compounds according to the invention are present as mixtures of different possible isomeric forms, in particular of stereoisomers, such as, for example, E and Z, cis or trans, threo and erythro, and also optical isomers. What is described and claimed are both the E and the Z isomers, and also the threo and erythro isomers, the optical isomers, and any mixtures of these isomers, tautomers.

The invention preferably provides compounds of the formula (Ia)



(Ia)

in which

$R^1$, $R^2$, and $R^3$ are identical or different and independently of one another represent hydrogen, fluorine, chlorine, bromine, cyano, nitro, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-pentyl, n-hexyl, n-heptyl, methoxy, ethoxy, n- or i-propoxy, methylthio, ethylthio, n- or i-propylthio, methylsulfinyl, ethylsulfinyl, methylsulfonyl or ethylsulfonyl, trifluoromethyl, trifluoroethyl, difluoromethoxy, trifluoromethoxy, difluorochloromethoxy, trifluoroethoxy, difluoromethylthio, difluorochloromethylthio, trifluoromethylthio, trifluoromethylsulfinyl or trifluoromethylsulfonyl, dimethylamino, diethylamino, acetyl, propionyl, methoxycarbonyl, ethoxycarbonyl, hydroximinomethyl, hydroximinoethyl, methoximinomethyl, ethoximinomethyl, methoximinoethyl or ethoximinoethyl, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, or

$R^1$ and $R^2$ together with the carbon atoms to which they are attached form a carbocyclic ring having 5 or 6 ring members,

where $R^1$, $R^2$, and $R^3$ do not simultaneously represent hydrogen,

$R^{4a}$ represents hydrogen, fluorine, chlorine, bromine, cyano, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-pentyl, n-hexyl, n-heptyl, allyl, propargyl or trifluoromethyl,

$R^5$ and $R^6$ are identical or different and independently of one another represent methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-pentyl, n-hexyl, n-heptyl,

allyl, methylallyl, crotonyl, propynyl or butynyl or cyanomethyl,

or represent optionally hydrogen-, fluorine-, chlorine-, bromine-, cyano-, nitro-, methyl-, ethyl-, n- or i-propyl-, n-, i-, s- or t-butyl-, n-pentyl-, n-hexyl-, n-heptyl-, methoxy-, ethoxy-, n- or i-propoxy-, methylthio-, ethylthio-, n- or i-propylthio-, methylsulfinyl-, ethylsulfinyl-, methylsulfonyl- or ethylsulfonyl-, trifluoromethyl-, trifluoroethyl-, difluoromethoxy-, trifluoromethoxy-, difluorochloromethoxy-, trifluoroethoxy-, difluoromethylthio-, difluorochloromethylthio-, trifluoromethylthio-, trifluoromethylsulfinyl- or trifluoromethylsulfonyl-, acetyl-, propionyl-, methoxycarbonyl-, ethoxycarbonyl-, hydroximinomethyl-, hydroximinoethyl-, methoximinomethyl-, ethoximinomethyl-, methoximinoethyl- or ethoximinoethyl-, cyclopropyl-, cyclobutyl-, cyclopentyl- or cyclohexyl-substituted benzyl,

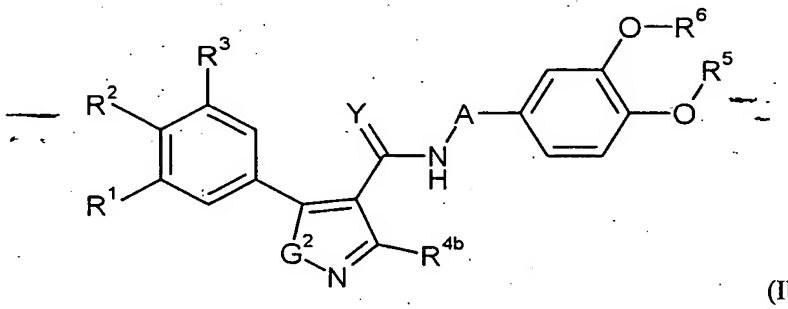
A represents methanediyl, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,3-diyl, propane-2,2-diyl, butane-1,1-diyl, butane-1,2-diyl, butane-1,3-diyl, butane-1,4-diyl, butane-2,2-diyl, butane-2,3-diyl, 1,1-diethylethane-1,2-diyl, cyclopropane-1,1-diyl or cyclopropane-1,2-diyl,

Y represents oxygen or sulfur and

$G^1$ represents oxygen, sulfur or N-$R^{7a}$, where

$R^{7a}$ represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

The invention likewise preferably provides compounds of the formula (Ib),



(Ib)

in which

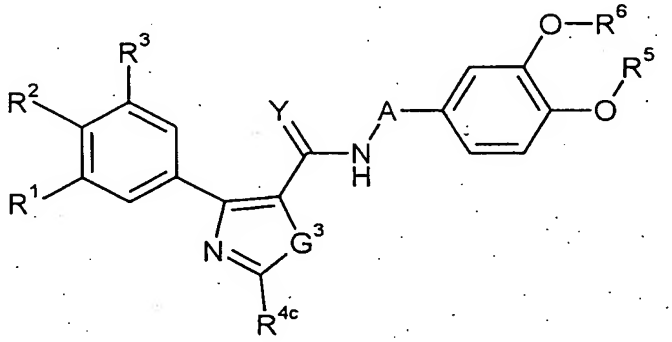
A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ und Y are as defined as stated as being preferred for A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y in formula (1a),

$R^{4b}$ represents hydrogen, fluorine, chlorine, bromine, cyano, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-pentyl, n-hexyl, n-heptyl, allyl, propargyl or trifluoromethyl,

$G^2$ represents oxygen, sulfur or N-$R^{7b}$, where

$R^{7b}$ represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

The invention furthermore preferably provides compounds of the formula (Ic),



(Ic)

in which

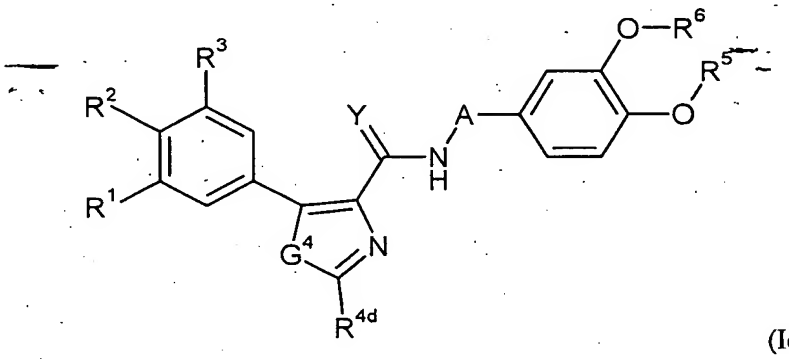
A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y are as defined as stated as being preferred for A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y in formula (1a),

$R^{4c}$ represents hydrogen, fluorine, chlorine, bromine, cyano, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-pentyl, n-hexyl, n-heptyl, allyl, propargyl or trifluoromethyl,

$G^3$ represents oxygen, sulfur or N-$R^{7c}$, where

$R^{7c}$ represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

The invention furthermore preferably provides compounds of the formula (Id),



(Id)

in which

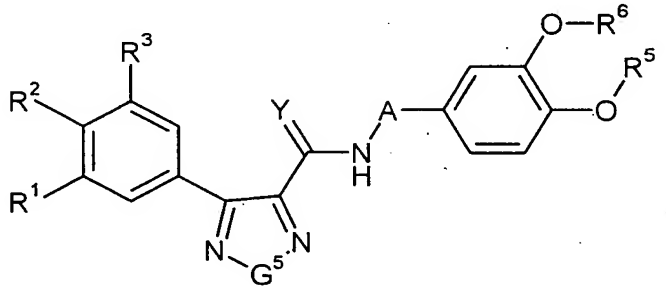
A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y are as defined as stated as being preferred for A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y in formula (1a),

$R^{4d}$ represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl,

$G^4$ represents oxygen, sulfur or N-$R^{7d}$, where

$R^{7d}$ represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

The invention furthermore preferably provides compounds of the formula (Ie),



(Ie)

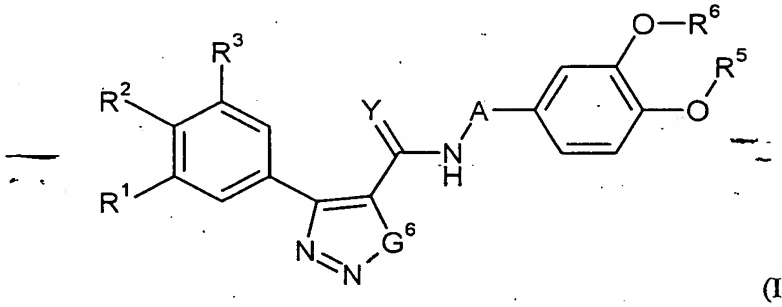
in which

A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y are as defined as stated as being preferred for A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y in formula (1a),

$G^5$ represents oxygen, sulfur or N-$R^{7e}$, where

$R^{7e}$ represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

The invention furthermore preferably provides compounds of the formula (If),



(If)

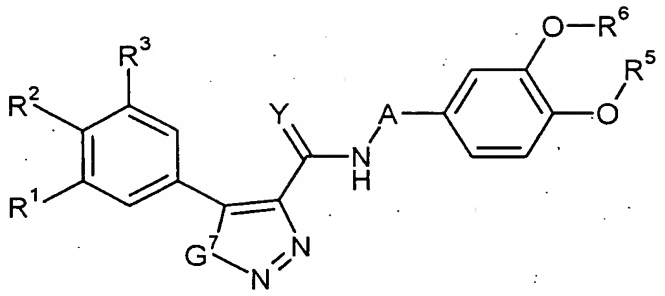
in which

A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y are as defined as stated as being preferred for A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y in formula (1a),

$G^6$ represents oxygen, sulfur or N-$R^{7f}$, where

$R^{7f}$ represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

The invention furthermore preferably provides compounds of the formula (Ig),



(Ig)

in which

A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y are as defined as stated as being preferred for A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y in formula (1a),

$G^7$ represents oxygen, sulfur or N-$R^{7g}$, where

$R^{7g}$ represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

In the formulae (Ia), (Ib), (Ic), (Id), (Ie), (If), (Ig), A, $R^1$, $R^2$, $R^3$, $R^5$, $R^6$ and Y have the following particularly preferred meanings:

$R^1$, $R^2$, and $R^3$ are identical or different and independently of one another also particularly preferably represent hydrogen, fluorine, chlorine, bromine, cyano, nitro, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-pentyl, n-hexyl, n-heptyl, methoxy, ethoxy, n- or i-propoxy, methylthio, ethylthio, n- or i-propylthio, methylsulfinyl, ethylsulfinyl, methylsulfonyl or ethylsulfonyl, trifluoromethyl, trifluoroethyl, difluoromethoxy, trifluoromethoxy, difluorochloromethoxy, trifluoroethoxy, difluoromethylthio, difluorochloromethylthio, trifluoromethylthio, trifluoromethylsulfinyl or trifluoromethylsulfonyl, dimethylamino, diethylamino, acetyl, propionyl, methoxycarbonyl, ethoxycarbonyl, hydroximinomethyl, hydroximinoethyl, methoximinomethyl, ethoximinomethyl, methoximinoethyl or ethoximinoethyl, cyclopropyl, cyclobutyl, cyclopentyl or cyclohexyl, or

$R^1$ and $R^2$ together with the carbon atoms to which they are attached form a carbocyclic ring having 5 or 6 ring members.

$R^1$, $R^2$, and $R^3$ do not simultaneously represent hydrogen.

A particularly preferably represents methanediyl, ethane-1,1-diyl, ethane-1,2-diyl, propane-1,1-diyl, propane-1,2-diyl, propane-1,3-diyl or propane-2,2-diyl.

Y particularly preferably represents oxygen.

$R^5$ and $R^6$ are identical or different and independently of one another particularly preferably

represent methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-pentyl, n-hexyl, n-heptyl, allyl, methylallyl, crotonyl, propynyl or butynyl or cyanomethyl.

In formula (Ia)

$R^{4a}$ particularly preferably represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-heptyl, trifluoromethyl, chlorine or cyano and

$G^1$ especially preferably represents oxygen, sulfur or N-$R^{7a}$, where

$R^{7a}$ particularly preferably represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

In formula (Ib)

$R^{4b}$ particularly preferably represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, trifluoromethyl, chlorine or cyano and

$G^2$ particularly preferably represents oxygen, sulfur or N-$R^{7b}$, where

$R^{7b}$ particularly preferably represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

In formula (Ic)

$R^{4c}$ particularly preferably represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-heptyl, trifluoromethyl, chlorine or cyano and

$G^3$ particularly preferably represents oxygen, sulfur or N-$R^{7c}$, where

$R^{7c}$ particularly preferably represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

In formula (Id)

$R^{4d}$ particularly preferably represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl, n-heptyl, trifluoromethyl, chlorine or cyano and

$G^4$ particularly preferably represents oxygen, sulfur or N-$R^{7d}$, where

$R^{7d}$ particularly preferably represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

In formula (Ie)

$G^5$ particularly preferably represents oxygen, sulfur or N-$R^{7e}$, where

$R^{7e}$ particularly preferably represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

In formula (If)

$G^6$ particularly preferably represents oxygen, sulfur or N-$R^{7f}$, where

$R^{7f}$ particularly preferably represents hydrogen, methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

In formula (Ig)

$G^7$ especially preferably represents oxygen, sulfur or N-$R^{7g}$, where

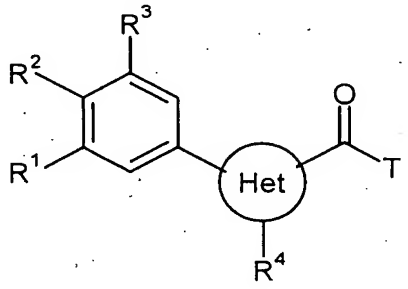
$R^{7g}$ particularly preferably represents methyl, ethyl, n- or i-propyl, n-, i-, s- or t-butyl.

The general or preferred radical definitions given above apply both to the end products of the formula (I) and, correspondingly, to the starting materials or intermediates required in each case for the preparation.

The radical definitions given in the particular combinations or preferred combinations of radicals specifically for these radicals are, independently of the respective given combination, also replaced by any radical definitions of other preferred ranges.

Finally, it has been found that the amides of the general formula (I) are obtained when

a) carboxylic acid derivatives of the general formula (II)



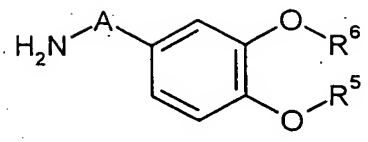

(II)

in which

$R^1$, $R^2$, $R^3$ and $R^4$ are as defined above and

T represents hydroxyl, halogen or alkoxy,

are reacted with an amine of the general formula (III)



(III)

in which

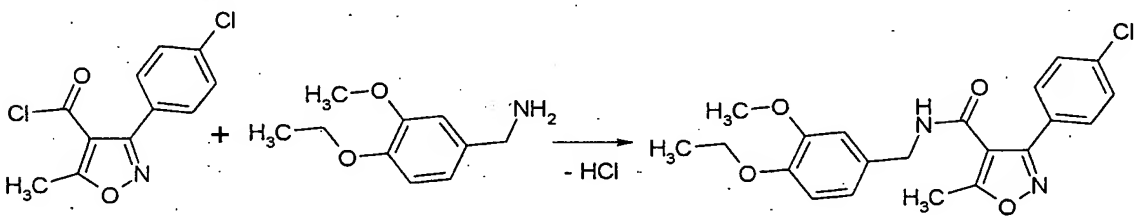
$R^5$, $R^6$ and A are as defined above,

- or an acid addition complex thereof -

if appropriate in the presence of an acid acceptor, if appropriate in the presence of a condensing agent, if appropriate in the presence of a catalyst and if appropriate in the presence of a diluent, or when

b) amides of the formula (I) where Y is oxygen are reacted with a sulfurizing agent, if appropriate in the presence of a diluent.

Using, for example, 3-(4-chlorophenyl)-5-methylisoxazole-4-carbonyl chloride and (4-ethoxy-3-methoxybenzyl)amine as starting materials, the course of the process (a) according to the invention can be illustrated by the formula scheme below:



The formula (II) provides a general definition of the carboxylic acid derivatives required as starting materials for carrying out the process a) according to the invention. In this formula (II), $R^1$, $R^2$, $R^3$ and $R^4$ preferably and in particular have those meanings which have already been mentioned in connection with the description of the compounds of the formula (I) according to the invention as being preferred and particularly preferred, respectively, for $R^1$, $R^2$, $R^3$ and $R^4$; T preferably represents alkoxy having 1 to 4 carbon atoms, in particular methoxy or ethoxy, represents hydroxyl or chlorine.

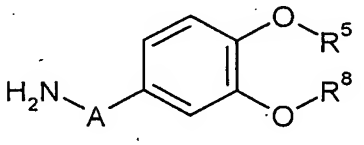
The starting materials of the formula (II) are known and/or can be prepared by processes known per se (compare, for example, J. Org. Chem. 27 (1962) 4305; J. Chem. Soc. (1963) 5838; J. Chem. Soc. (1963) 5845; Chem. Ber. 106, 3275 (1973); US 3,479,365; US 3,551,440; J. Org. Chem. (1967) 32(10) 3132; Tetrahedron 25, (1969), 389; Synthetic Com. (1987), 17(2), 165; EP 352581; EP 352581; EP 1186598; Bioor.&Medicinal Chem. Lett., 11(5),641(2001); JP 20011011060; JP 2001011059; EP 352581; Tet. Lett. 23,(2), 235 (1982); J. of Org. Chem. 55(13), 4011 (1990);

EP 352581; EP 3252581; Synthesis, (1), 64 (1996); GB 1,058,384; US 3,257,411; J. Am. Chem. Soc. (1969), 89(21), 5462; J. Org. Chem. (1967), 27, 4305; US4,380,465; Chem.Ber. 105, (1972) 196; Tetrahedron Letters 17, (1971), 1281; WO95/04724; CH 502365; EP 785193; Heterocycles (2000), 53(1), 159; Aust. J. Chem. (1994), 47,1375; Bulletin des Soc. Chim. Belges (1996), 105(1), 33; Bulletin des Soc. Chim. Belges (1996), 105(4),189).

The formula (III) provides a general definition of the amines furthermore required as starting materials for carrying out the process a) according to the invention. In this formula (III), A, $R^5$ and $R^6$ preferably and in particular have those meanings which have already been mentioned in connection with the description of the compounds of the formula (I) according to the invention as being preferred and as being particularly preferred, respectively, for $R^5$ and $R^6$.

Some of the amines of the formula (III) are known organic chemicals for synthesis and/or can be prepared by processes known per se.

Novel and also part of the subject matter of the invention are amines of the formulae (III-a)



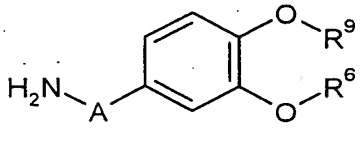
(III-a)

in which

A and $R^5$ are as defined above and

$R^8$ represents allyl, propargyl, 2-butynyl or cyanomethyl

and (III-b)



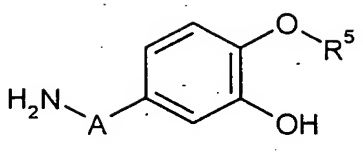
(III-b)

in which

A and $R^6$ are as defined above and

$R^9$ represents allyl, propargyl, 2-butynyl or cyanomethyl.

The amines of the formulae (III-a) and (III-b) are obtained (process c) when hydroxyl compounds of the general formula (IV-a)

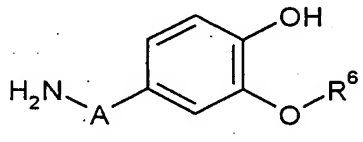


(IV-a)

in which

A and $R^5$ are as defined above

or hydroxyl compounds of the general formula (IV-b)



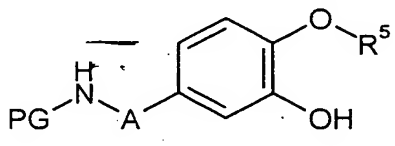
(IV-b)

in which

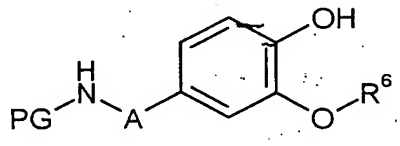
A and $R^6$ are as defined above,

are reacted with allyl chloride, allyl bromide or allyl iodide, propargyl chloride, propargyl bromide or propargyl iodide, 2-butynyl chloride, 2-butynyl bromide or 2-butynyl iodide or chloro-, bromo- or iodoacetonitrile, if appropriate in the presence of a diluent, such as, for example, acetonitrile, and if appropriate in the presence of an acid acceptor, such as, for example, potassium carbonate.

Prior to the alkylation, the amino group of the compounds of the formula (IV-a) and (IV-b) is, if appropriate, provided with a protective group customary for amines, such as, for example, t-butoxy-carbonyl, using customary methods. In this manner, compounds of the formula (IV-a*), or (IV-b*)



(IV-a*)



(IV-b*)

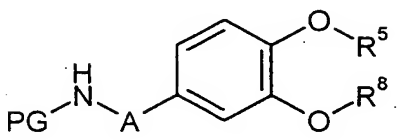
in which

$R^5$ and $R^6$ are as defined above and

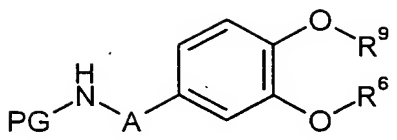
PG represents the protective group

are formed.

After the alkylation reaction, which initially yields compounds of the formula (III-a*) or (III-b*)



(III-a*)



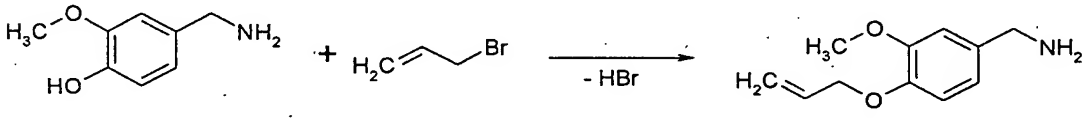
(III-b*)

in which

$R^8$, $R^9$, PG, and $R^5$ and $R^6$ are as defined above,

the protective group is removed again using customary methods (see also the Preparation Examples).

Using, for example, 4-(aminomethyl)-2-methoxyphenol and allyl bromide as starting materials, the course of the process c) according to the invention can be illustrated by the formula scheme below:




The formula (IV-a) provides a general definition of the hydroxyl compounds required as starting materials for carrying out the process c) according to the invention. In this formula (IV-a), $R^5$ preferably and in particular has that meaning which has already been mentioned in connection with the description of the compounds of the formula (I) according to the invention as being preferred and as being particularly preferred, respectively, for $R^5$.

The hydroxyl compounds of the formula (IV-a) are commercial chemicals for synthesis or can be obtained by known methods (compare, for example, J. Chem. Soc. 127 (1925), 560 and J. Amer. Chem. Soc. 72 (1950), 2781; JP 11130739 or DE 19958165).

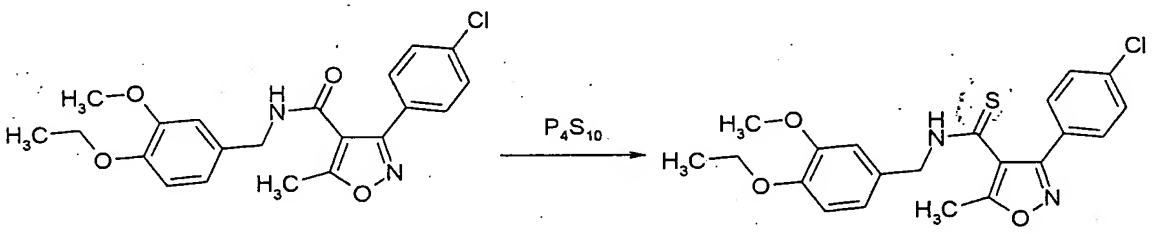
The formula (IV-b) provides a general definition of the hydroxyl compounds alternatively required as starting materials for carrying out the process c) according to the invention. In this formula (IV-b), $R^6$ preferably and in particular has that meaning which has already been mentioned in connection with the description of the compounds of the formula (I) according to the invention as being preferred and as being particularly preferred, respectively, for $R^6$.

The hydroxyl compounds of the formula (IV-b) are commercial chemicals for synthesis or can be obtained by known methods (compare, for example, Ger. Offen, 4322065; J. Org. Chem., 53(5), 1064-71 (1988); Synth. Comm., 7(1), 71-8 (1977)).

The compounds allyl chloride, allyl bromide or allyl iodide, propargyl chloride, propargyl bromide or propargyl iodide, 2-butynyl chloride, 2-butynyl bromide or 2-butynyl iodide or chloro-, bromo- or iodoacetonitrile furthermore required as starting materials for carrying out the process c) according

to the invention are generally customary chemicals for synthesis.

Using, for example, 3-(4-chlorophenyl)-N-(4-ethoxy-3-methoxybenzyl)-5-methylisoxazole-4-carboxamide and phosphorus pentasulfide as starting materials, the course of the process b) according to the invention can be illustrated by the formula scheme below:




The amides required as starting materials for carrying out the process b) according to the invention are compounds according to the invention and can be obtained by the process a) according to the invention.

Suitable sulfurizing agents for carrying out the process b) according to the invention are all reagents capable of exchanging oxygen atoms attached to carbon for sulfur atoms, such as, for example, hydrogen sulfide, phosphorus pentasulfide or Lawesson's reagent.

Hydrogen sulfide, phosphorus pentasulfide or Lawesson's reagent are commercial chemicals for synthesis.

The process a) according to the invention is, if appropriate, carried out in the presence of a diluent. Suitable diluents are water and organic solvents. These include in particular aliphatic, alicyclic or aromatic, optionally halogenated hydrocarbons, such as, for example, benzine, benzene, toluene, xylene, chlorobenzene, dichlorobenzene, petroleum ether, hexane, cyclohexane, dichloromethane, chloroform, carbon tetrachloride; ethers, such as diethyl ether, diisopropyl ether, dioxane, tetrahydrofuran or ethylene glycol dimethyl ether or ethylene glycol diethyl ether; ketones, such as acetone, butanone or methyl isobutyl ketone; nitriles, such as acetonitrile, propionitrile or benzonitrile; amides, such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylformanilide, N-methylpyrrolidone or hexamethylphosphoric triamide; esters, such as methyl acetate, or ethyl acetate, sulfoxides, such as dimethyl sulfoxide, alcohols, such as methanol, ethanol, n- or i-propanol, ethylene glycol, ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, mixtures thereof with water or pure water.

The process a) according to the invention is, if appropriate, carried out in the presence of a suitable acid acceptor. Suitable acid acceptors are all customary inorganic or organic bases. These include, for example, alkali metal or alkaline earth metal hydrides, hydroxides, amides, alkoxides, acetates, carbonates or bicarbonates, such as, for example, sodium hydride, sodium amide, sodium methoxide,

sodium ethoxide, potassium tert-butoxide, sodium hydroxide, potassium hydroxide, ammonium hydroxide, sodium acetate, potassium acetate, calcium acetate, ammonium acetate, sodium carbonate, potassium carbonate, potassium bicarbonate, sodium bicarbonate or ammonium carbonate, and also tertiary amines, such as trimethylamine, triethylamine, tributylamine, N,N-dimethylaniline, N,N-dimethylbenzylamine, pyridine, N-methylpiperidine, N,N-dimethylaminopyridine, diazabicyclooctane (DABCO), diazabicyclononene (DBN) or diazabicycloundecene (DBU).

The process a) according to the invention is, if appropriate, carried out in the presence of a suitable condensing agent. Suitable condensing agents are all condensing agents customarily used for such amidation reactions. Acid halide formers, such as phosgene, phosphorus tribromide, phosphorus trichloride, phosphorus pentachloride, phosphorus oxychloride or thionyl chloride; anhydride formers, such as ethyl chloroformate, methyl chloroformate, isobutyl chloroformate or methanesulfonyl chloride; carbodiimides, such as N,N'-dicyclohexylcarbodiimide (DCC) or other customary condensing agents, such as phosphorus pentoxide, polyphosphoric acid, N,N'-carbonyldiimidazole, 2-ethoxy-N-ethoxycarbonyl-1,2-dihydroquinoline (EEDQ) or triphenylphosphine/-carbon tetrachloride may be mentioned by way of example.

The process a) according to the invention is, if appropriate, carried out in the presence of a catalyst. 4-Dimethylaminopyridine, 1-hydroxybenzotriazole or dimethylformamide may be mentioned by way of example.

When carrying out the process a) according to the invention, the reaction temperatures may be varied within a relatively wide range. In general, the process is carried out at temperatures between -50°C and +150°C, preferably at temperatures between -20°C and 150°C.

For carrying out the process a) according to the invention, in general from 1 to 5 mol, preferably from 1.0 to 2.5 mol, of amine are employed per mole of carboxylic acid derivative of the formula (II).

The process a) according to the invention can also be carried out as a two-step process. Here, the carboxylic acid derivatives of the general formula (II) are initially converted into an activated form and, in a subsequent step, reacted with the amines of the general formula (III) to give the amides of the general formula (I) according to the invention.

Suitable activated forms of the carboxylic acid derivatives of the formula (II) are all carboxy-activated derivatives, such as, for example, acid halides, preferably acid chlorides, acid azides, furthermore symmetrical and mixed anhydrides, such as, for example, the mixed o-alkyl carbonic anhydrides, furthermore activated esters, such as, for example, p-nitrophenyl esters or N-hydroxy-succinimide esters, and also adducts with condensing agents, such as, for example, dicyclohexyl

carbodiimide or activated forms, generated in situ, of the carboxylic acids.

Suitable diluents for carrying out the process b) according to the invention are all inert organic solvents. These preferably include aliphatic, alicyclic or aromatic hydrocarbons, such as, for example, petroleum ether, hexane, heptane, cyclohexane, methylcyclohexane, benzene, toluene, xylene or decalin; halogenated hydrocarbons, such as, for example, chlorobenzene, dichlorobenzene, dichloromethane, chloroform, carbon tetrachloride, dichloroethane or trichloroethane; ethers, such as diethyl ether, diisopropyl ether, methyl t-butyl ether, methyl t-amyl ether, dioxane, tetrahydrofuran, 1,2-dimethoxyethane, 1,2-diethoxyethane or anisole.

When carrying out the process b) according to the invention, the reaction temperatures can be varied within a relatively wide range. In general, the process is carried out at temperatures of from 0°C to 150°C, preferably at temperatures of from 0°C to 80°C.

For carrying out the process b) according to the invention for preparing the compounds of the formula (I), in general from 0.1 to 15 mol, preferably from 0.5 to 8 mol, of sulfurizing agent are employed per mole of the amide of the formula (I) where Y represents oxygen.

The practice of the reaction and the work-up and isolation of the reaction products are carried out by known processes (compare also the Preparation Examples).

The processes according to the invention are generally carried out under atmospheric pressure. However, it is also possible to operate under elevated or reduced pressure – in general between 0.1 bar and 10 bar.

The practice of the reaction and the work-up and isolation of the reaction products are carried out by known processes.

The compounds according to the invention have potent microbicidal activity and can be employed for controlling unwanted microorganisms, such as fungi and bacteria, in crop protection and in the protection of materials.

Fungicides can be employed in crop protection for controlling Plasmodiophoromycetes, Oomycetes, Chytridiomycetes, Zygomycetes, Ascomycetes, Basidiomycetes and Deuteromycetes.

Bactericides can be employed in crop protection for controlling Pseudomonadaceae, Rhizobiaceae, Enterobacteriaceae, Corynebacteriaceae and Streptomycetaceae.

Some pathogens causing fungal and bacterial diseases which come under the generic names listed above may be mentioned as examples, but not by way of limitation:

Xanthomonas species, such as, for example, Xanthomonas campestris pv. oryzae;

Pseudomonas species, such as, for example, Pseudomonas syringae pv. lachrymans;

Erwinia species, such as, for example, Erwinia amylovora;

Pythium species, such as, for example, Pythium ultimum;

Phytophthora species, such as, for example, Phytophthora infestans;

Pseudoperonospora species, such as, for example, Pseudoperonospora humuli or Pseudoperonospora cubensis;

Plasmopara species, such as, for example, Plasmopara viticola;

Bremia species, such as, for example, Bremia lactucae;

Peronospora species, such as, for example, Peronospora pisi or P. brassicae;

Erysiphe species, such as, for example, Erysiphe graminis;

Sphaerotheca species, such as, for example, Sphaerotheca fuliginea;

Podosphaera species, such as, for example, Podosphaera leucotricha;

Venturia species, such as, for example, Venturia inaequalis;

Pyrenophora species, such as, for example, Pyrenophora teres or P. graminea (conidia form: Drechslera, syn: Helminthosporium);

Cochliobolus species, such as, for example, Cochliobolus sativus (conidia form: Drechslera, syn: Helminthosporium);

Uromyces species, such as, for example, Uromyces appendiculatus;

Puccinia species, such as, for example, Puccinia recondita;

Sclerotinia species, such as, for example, Sclerotinia sclerotiorum;

Tilletia species, such as, for example, Tilletia caries;

Ustilago species, such as, for example, Ustilago nuda or Ustilago avenae;

Pellicularia species, such as, for example, Pellicularia sasakii;

Pyricularia species, such as, for example, Pyricularia oryzae;

Fusarium species, such as, for example, Fusarium culmorum;

Botrytis species, such as, for example, Botrytis cinerea;

Septoria species, such as, for example, Septoria nodorum;

Leptosphaeria species, such as, for example, Leptosphaeria nodorum;

Cercospora species, such as, for example, Cercospora canescens;

Alternaria species, such as, for example, Alternaria brassicae; and

Pseudocercosporella species, such as, for example, Pseudocercosporella herpotrichoides.

The active compounds according to the invention also show a strong invigorating action in plants. Accordingly, they are suitable for mobilizing the internal defenses of the plant against attack by unwanted microorganisms.

In the present context, plant-invigorating (resistance-inducing) compounds are to be understood as meaning substances which are capable of stimulating the defense system of plants such that, when the treated plants are subsequently inoculated with unwanted microorganisms, they display substantial resistance to these microorganisms.

In the present case, unwanted microorganisms are to be understood as meaning phytopathogenic fungi, bacteria and viruses. The compounds according to the invention can thus be used to protect plants within a certain period of time after treatment against attack by the pathogens mentioned. The period of time for which this protection is achieved generally extends for 1 to 10 days, preferably 1

to 7 days, from the treatment of the plants with the active compounds.

The fact that the active compounds are well tolerated by plants at the concentrations required for controlling plant diseases permits the treatment of above-ground parts of plants, of propagation stock and seeds, and of the soil.

The active compounds according to the invention can be employed with particularly good results for controlling diseases in viticulture and in the cultivation of fruit and vegetables, such as, for example, against Alternaria, Phytophtora and Plasmopara species.

The active compounds according to the invention are also suitable for increasing the yield of crops. In addition, they show reduced toxicity and are well tolerated by plants.

If appropriate, the active compounds according to the invention can, at certain concentrations and application rates, also be employed as herbicides, for regulating plant growth and for controlling animal pests. If appropriate, they can also be used as intermediates or precursors in the synthesis of other active compounds.

According to the invention, it is possible to treat all plants and parts of plants. Plants are to be understood here as meaning all plants and plant populations, such as desired and undesired wild plants or crop plants (including naturally occurring crop plants). Crop plants can be plants which can be obtained by conventional breeding and optimization methods or by biotechnological and genetic engineering methods or combinations of these methods, including the transgenic plants and including plant cultivars which can or cannot be protected by plant breeders' certificates. Parts of plants are to be understood as meaning all above-ground and below-ground parts and organs of plants, such as shoot, leaf, flower and root, examples which may be mentioned being leaves, needles, stems, trunks, flowers, fruit-bodies, fruits and seeds and also roots, tubers and rhizomes. Parts of plants also include harvested material and vegetative and generative propagation material, for example seedlings, tubers, rhizomes, cuttings and seeds.

The treatment of the plants and parts of plants according to the invention with the active compounds is carried out directly or by action on their environment, habitat or storage area according to customary treatment methods, for example by dipping, spraying, evaporating, atomizing, broadcasting, brushing-on and, in the case of propagation material, in particular in the case of seeds, furthermore by one- or multilayer coating.

In the protection of materials, the compounds according to the invention can be employed for protecting industrial materials against infection with, and destruction by, unwanted microorganisms.

Industrial materials in the present context are understood as meaning non-living materials which have been prepared for use in industry. For example, industrial materials which are intended to be

protected by active compounds according to the invention from microbial change or destruction can be tackifiers, sizes, paper and board, textiles, leather, wood, paints and plastic articles, cooling lubricants and other materials which can be infected with, or destroyed by, microorganisms. Parts of production plants, for example cooling-water circuits, which may be impaired by the proliferation of microorganisms may also be mentioned within the scope of the materials to be protected. Industrial materials which may be mentioned within the scope of the present invention are preferably adhesives, sizes, paper and board, leather, wood, paints, cooling lubricants and heat-transfer liquids, particularly preferably wood.

Microorganisms capable of degrading or changing the industrial materials which may be mentioned are, for example, bacteria, fungi, yeasts, algae and slime organisms. The active compounds according to the invention preferably act against fungi, in particular molds, wood-discoloring and wood-destroying fungi (Basidiomycetes) and against slime organisms and algae.

Microorganisms of the following genera may be mentioned as examples:

Alternaria, such as Alternaria tenuis,

Aspergillus, such as Aspergillus niger,

Chaetomium, such as Chaetomium globosum,

Coniophora, such as Coniophora puetana,

Lentinus, such as Lentinus tigrinus,

Penicillium, such as Penicillium glaucum,

Polyporus, such as Polyporus versicolor,

Aureobasidium, such as Aureobasidium pullulans,

Sclerophoma, such as Sclerophoma pityophila,

Trichoderma, such as Trichoderma viride,

Escherichia, such as Escherichia coli,

Pseudomonas, such as Pseudomonas aeruginosa, and

Staphylococcus, such as Staphylococcus aureus.

Depending on their particular physical and/or chemical properties, the active compounds can be converted into the customary formulations, such as solutions, emulsions, suspensions, powders, foams, pastes, granules, aerosols and microencapsulations in polymeric substances and in coating compositions for seeds, and ULV cool and warm fogging formulations.

These formulations are produced in a known manner, for example by mixing the active compounds with extenders, that is liquid solvents, liquefied gases under pressure, and/or solid carriers, optionally with the use of surfactants, that is emulsifiers and/or dispersants, and/or foam formers. If the extender used is water, it is also possible to employ, for example, organic solvents as auxiliary solvents. Essentially, suitable liquid solvents are: aromatics such as xylene, toluene or alkylnaphthalenes, chlorinated aromatics or chlorinated aliphatic hydrocarbons such as chlorobenzenes, chloroethylenes or methylene chloride, aliphatic hydrocarbons such as cyclohexane or paraffins, for example petroleum fractions, alcohols such as butanol or glycol and their ethers and esters, ketones such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents such as dimethylformamide or dimethyl sulfoxide, or else water. Liquefied gaseous extenders or carriers are to be understood as meaning liquids which are gaseous at standard temperature and under atmospheric pressure, for example aerosol propellants such as halogenated hydrocarbons, or else butane, propane, nitrogen and carbon dioxide. Suitable solid carriers are: for example ground natural minerals such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals such as finely divided silica, alumina and silicates. Suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as calcite, pumice, marble, sepiolite and dolomite, or else synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust, coconut shells, corn cobs and tobacco stalks. Suitable emulsifiers and/or foam formers are: for example nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulfonates, alkyl sulfates, arylsulfonates, or else protein hydrolysates. Suitable dispersants are: for example lignosulfite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose, natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, or else natural phospholipids such as cephalins and lecithins and synthetic phospholipids can be used in the formulations. Other possible additives are mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations generally comprise between 0.1 and 95 per cent by weight of active compound, preferably between 0.5 and 90%.

The active compounds according to the invention can, as such or in their formulations, also be used in a mixture with known fungicides, bactericides, acaricides, nematicides or insecticides, to broaden, for example, the activity spectrum or to prevent development of resistance. In many cases, synergistic effects are obtained, i.e. the activity of the mixture is greater than the activity of the individual components.

Suitable mixing components are, for example, the following compounds:

**Fungicides:**

2-phenylphenol; 8-hydroxyquinoline sulfate; acibenzolar-S-methyl; aldimorph; amidoflumet; ampropylfos; ampropylfos-potassium; andoprim; anilazine; azaconazole; azoxystrobin; benalaxyl; benalaxyl-M; benodanil; benomyl; benthiavalicarb-isopropyl; benzamacril; benzamacril-isobutyl; bilanafos; binapacryl; biphenyl; bitertanol; blasticidin-S; boscalid; bromuconazole; bupirimate; buthiobate; butylamine; calcium polysulfide; capsimycin; captafol; captan; carbendazim; carboxin; carpropamid; carvone; chinomethionat; chlobenthiazone; chlorfenazole; chloroneb; chlorothalonil; chlozolinate; clozylacon; cyazofamid; cyflufenamid; cymoxanil; cyproconazole; cyprodinil; cyprofuram; Dagger G; debacarb; dichlofluanid; dichlone; dichlorophen; diclocymet; diclomezine; dicloran; diethofencarb; difenoconazole; diflumetorim; dimethirimol; dimethomorph; dimoxystrobin; diniconazole; diniconazole-M; dinocap; diphenylamine; dipyrithione; ditalimfos; dithianon; dodine; drazoxolon; edifenphos; epoxiconazole; ethaboxam; ethirimol; etridiazole; famoxadone; fenamidone; fenapanil; fenarimol; fenbuconazole; fenfuram; fenhexamid; fenitropan; fenoxanil; fenpiclonil; fenpropidin; fenpropimorph; ferbam; fluazinam; flubenzimine; fludioxonil; flumetover; flumorph; fluoromide; fluoxastrobin; fluquinconazole; flurprimidol; flusilazole; flusulfamide; flutolanil; flutriafol; folpet; fosetyl-Al; fosetyl-sodium; fuberidazole; furalaxyl; furametpyr; furcarbanil; furmecyclox; guazatine; hexachlorobenzene; hexaconazole; hymexazole; imazalil; imibenconazole; iminoctadine triacetate; iminoctadine tris(albesilate); iodocarb; ipconazole; iprobenfos; iprodione; iprovalicarb; irumamycin; isoprothiolane; isovaledione; kasugamycin; kresoxim-methyl; mancozeb; maneb; meferimzone; mepanipyrim; mepronil; metalaxyl; metalaxyl-M; metconazole; methasulfocarb; methfuroxam; metiram; metominostrobin; metsulfovax; mildiomycin; myclobutanil; myclozolin; natamycin; nicobifen; nitrothal-isopropyl; noviflumuron; nuarimol; ofurace; orysastrobin; oxadixyl; oxolinic acid; oxpoconazole; oxycarboxin; oxyfenthiin; paclobutrazole; pefurazoate; penconazole; pencycuron; phosdiphen; phthalide; picoxystrobin; piperalin; polyoxins; polyoxorim; probenazole; prochloraz; procymidone; propamocarb; propanosine-sodium; propiconazole; propineb; proquinazid; prothioconazole; pyraclostrobin; pyrazophos; pyrifenox; pyrimethanil; pyroquilon; pyroxyfur; pyrrolenitrine; quinconazole; quinoxyfen; quintozene; simeconazole; spiroxamine; sulfur; tebuconazole; tecloftalam; tecnazene; tetcyclacis; tetraconazole;

thiabendazole; thicyofen; thifluzamide; thiophanate-methyl; thiram; tioxymid; tolclofos-methyl; tolylfluanid; triadimefon; triadimenol; triazbutil; triazoxide; tricyclamide; tricyclazole; tridemorph; trifloxystrobin; triflumizole; triforine; triticonazole; uniconazole; validamycin A; vinclozolin; zineb; ziram; zoxamide; (2S)-N-[2-[4-[[3-(4-chlorophenyl)-2-propynyl]oxy]-3-methoxyphenyl]ethyl]-3-methyl-2-[(methylsulfonyl)amino]-butanamide; 1-(1-naphthalenyl)-1H-pyrrole-2,5-dione; 2,3,5,6-tetrachloro-4-(methylsulfonyl)-pyridine; 2-amino-4-methyl-N-phenyl-5-thiazolecarboxamide; 2-chloro-N-(2,3-dihydro-1,1,3-trimethyl-1H-inden-4-yl)-3-pyridinecarboxamide; 3,4,5-trichloro-2,6-pyridinedicarbonitrile; actinovate; cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)cycloheptanol; methyl 1-(2,3-dihydro-2,2-dimethyl-1H-inden-1-yl)-1H-imidazole-5-carboxylate; monopotassium carbonate; N-(6-methoxy-3-pyridinyl)-cyclopropanecarboxamide; N-butyl-8-(1,1-dimethylethyl)-1-oxaspiro[4.5]decane-3-amine; sodium tetracarbonate;

and copper salts and preparations, such as Bordeaux mixture; copper hydroxide; copper naphthenate; copper oxychloride; copper sulfate; cufraneb; copper oxide; mancopper; oxine-copper.

**Bactericides:**

bronopol, dichlorophen, nitrapyrin, nickel dimethyldithiocarbamate, kasugamycin, octhilinone, furancarboxylic acid, oxytetracyclin, probenazole, streptomycin, tecloftalam, copper sulfate and other copper preparations.

**Insecticides / acaricides / nematicides:**

*1. Acetylcholinesterase (AChE) inhibitors*

1.1 carbamates (for example alanycarb, aldicarb, aldoxycarb, allyxycarb, aminocarb, azamethiphos, bendiocarb, benfuracarb, bufencarb, butacarb, butocarboxim, butoxycarboxim, carbaryl, carbofuran, carbosulfan, chloethocarb, coumaphos, cyanofenphos, cyanophos, dimetilan, ethiofencarb, fenobucarb, fenothiocarb, formetanate, furathiocarb, isoprocarb, metam-sodium, methiocarb, methomyl, metolcarb, oxamyl, pirimicarb, promecarb, propoxur, thiodicarb, thiofanox, triazamate, trimethacarb, XMC, xylylcarb)

1.2 organophosphates (for example acephate, azamethiphos, azinphos (-methyl, -ethyl), bromophos-ethyl, bromfenvinfos (-methyl), butathiofos, cadusafos, carbophenothion, chlorethoxyfos, chlorfen-vinphos, chlormephos, chlorpyrifos (-methyl/-ethyl), coumaphos, cyanofenphos, cyanophos, chlorfenvinphos, demeton-S-methyl, demeton-S-methylsulfone, dialifos, diazinon, dichlofenthion, dichlorvos/DDVP, dicrotophos, dimethoate, dimethylvinphos, dioxabenzofos, disulfoton, EPN, ethion, ethoprophos, etrimfos, famphur, fenamiphos, fenitrothion, fensulfothion, fenthion, flupyra-zofos, fonofos, formothion, fosmethilan, fosthiazate, heptenophos, iodofenphos, iprobenfos, isazofos, isofenphos, isopropyl o-salicylate, isoxathion, malathion, mecarbam, methacrifos, methamidophos, methidathion, mevinphos, monocrotophos, naled, omethoate, oxydemeton-methyl, parathion (-

methyl/-ethyl), phenthoate, phorate, phosalone, phosmet, phosphamidon, phosphocarb, phoxim, pirimiphos (-methyl/-ethyl), profenofos, propaphos, propetamphos, prothiofos, prothoate, pyraclofos, pyridaphenthion, pyridathion, quinalphos, sebufos, sulfotep, sulprofos, tebupirimfos, temephos, terbufos, tetrachlorvinphos, thiometon, triazophos, triclorfon, vamidothion)

*2. Sodium channel modulators/blockers of voltage-gated sodium channels*

2.1 pyrethroids (for example acrinathrin, allethrin (d-cis-trans, d-trans), beta-cyfluthrin, bifenthrin, bioallethrin, bioallethrin-S-cyclopentyl-isomer, bioethanomethrin, biopermethrin, bioresmethrin, chlovaporthrin, cis-cypermethrin, cis-resmethrin, cis-permethrin, clocythrin, cycloprothrin, cyfluthrin, cyhalothrin, cypermethrin (alpha-, beta-, theta-, zeta-), cyphenothrin, DDT, deltamethrin, empenthrin (1R-isomer), esfenvalerate, etofenprox, fenfluthrin, fenpropathrin, fenpyrithrin, fenvalerate, flubrocythrinate, flucythrinate, flufenprox, flumethrin, fluvalinate, fubfenprox, gamma-cyhalothrin, imiprothrin, kadethrin, lambda-cyhalothrin, metofluthrin, permethrin (cis-, trans-), phenothrin (1R-trans isomer), prallethrin, profluthrin, protrifenbute, pyresmethrin, resmethrin, RU 15525, silafluofen, tau-fluvalinate, tefluthrin, terallethrin, tetramethrin (1R-isomer), tralomethrin, transfluthrin, ZXI 8901, pyrethrins (pyrethrum))

2.2 oxadiazines (for example indoxacarb)

*3. Acetylcholine receptor agonists/antagonists*

3.1 chloronicotinyls/neonicotinoids (for example acetamiprid, clothianidin, dinotefuran, imidacloprid, nitenpyram, nithiazine, thiacloprid, thiamethoxam)

3.2 nicotine, bensultap, cartap

*4. Acetylcholine receptor modulators*

4.1 spinosyns (for example spinosad)

*5. Antagonists of GABA-gated chloride channels*

5.1 cyclodiene organochlorines (for example camphechlor, chlordane, endosulfan, gamma-HCH, HCH, heptachlor, lindane, methoxychlor

5.2 fiproles (for example acetoprole, ethiprole, fipronil, vaniliprole)

*6. Chloride channel activators*

6.1 mectins (for example abamectin, avermectin, emamectin, emamectin-benzoate, ivermectin, milbemectin, milbemycin)

*7. Juvenile hormone mimetics*

(for example diofenolan, epofenonane, fenoxycarb, hydroprene, kinoprene, methoprene, pyriproxifen, triprene)

*8. Ecdyson agonists/disruptors*

8.1 diacylhydrazines (for example chromafenozide, halofenozide, methoxyfenozide, tebufenozide)

*9. Chitin biosynthesis inhibitors*

9.1 benzoylureas (for example bistrifluron, chlofluazuron, diflubenzuron, fluazuron, flucycloxuron, flufenoxuron, hexaflumuron, lufenuron, novaluron, noviflumuron, penfluron, teflubenzuron, triflumuron)

9.2 buprofezin

9.3 cyromazine

*10. Inhibitors of oxidative phosphorylation, ATP disruptors*

10.1 diafenthiuron

10.2 organotins (for example azocyclotin, cyhexatin, fenbutatin-oxide)

*11. Decouplers of oxidative phosphorylation acting by interrupting the H-proton gradient*

11.1 pyrroles (for example chlorfenapyr)

11.2 dinitrophenols (for example binapacryl, dinobuton, dinocap, DNOC)

*12. Site-I electron transport inhibitors*

12.1 METIs (for example fenazaquin, fenpyroximate, pyrimidifen, pyridaben, tebufenpyrad, tolfenpyrad)

12.2 hydramethylnone

12.3 dicofol

*13. Site-II electron transport inhibitors*

13.1 rotenone

*14. Site-III electron transport inhibitors*

14.1 acequinocyl, fluacrypyrim

*15. Microbial disruptors of the insect gut membrane*

Bacillus thuringiensis strains

*16. Inhibitors of fat synthesis*

16.1 tetronic acids (for example spirodiclofen, spiromesifen)

16.2 tetramic acids [for example 3-(2,5-dimethylphenyl)-8-methoxy-2-oxo-1-azaspiro[4.5]dec-3-en-4-yl ethyl carbonate (alias: carbonic acid, 3-(2,5-dimethylphenyl)-8-methoxy-2-oxo-1-azaspiro[4.5]dec-3-en-4-yl ethyl ester, CAS Reg. No.: 382608-10-8) and carbonic acid, cis-3-(2,5-dimethylphenyl)-8-methoxy-2-oxo-1-azaspiro[4.5]dec-3-en-4-yl ethyl ester (CAS Reg. No.: 203313-25-1)]

*17. Carboxamides*

(for example flonicamid)

*18. Octopaminergic agonists*

(for example amitraz)

*19. Inhibitors of magnesium-stimulated ATPase*

(for example propargite)

*20. Phthalamides*

(for example $N^2$-[1,1-dimethyl-2-(methylsulfonyl)ethyl]-3-iodo-$N^1$-[2-methyl-4-[1,2,2,2-tetrafluoro-1-(trifluoromethyl)ethyl]phenyl]-1,2-benzenedicarboxamide (CAS Reg. No.: 272451-65-7), flubendiamide)

*21. Nereistoxin analogues*

(for example thiocyclam hydrogen oxalate, thiosultap-sodium)

*22. Biologicals, hormones or pheromones*

(for example azadirachtin, Bacillus spec., Beauveria spec., codlemone, Metarrhizium spec., Paecilomyces spec., thuringiensin, Verticillium spec.)

*23. Active compounds with unknown or unspecific mechanisms of action*

23.1 fumigants (for example aluminum phosphide, methyl bromide, sulfuryl fluoride)

23.2 selective antifeedants (for example cryolite, flonicamid, pymetrozine)

23.3 mite growth inhibitors (for example clofentezine, etoxazole, hexythiazox)

23.4 amidoflumet, benclothiaz, benzoximate, bifenazate, bromopropylate, buprofezin, chinomethionat, chlordimeform, chlorobenzilate, chloropicrin, clothiazoben, cycloprene, cyflumetofen, dicyclanil, fenoxacrim, fentrifanil, flubenzimine, flufenerim, flutenzin, gossyplure, hydramethylnone, japonilure, metoxadiazone, petroleum, piperonyl butoxide, potassium oleate, pyrafluprole, pyridalyl, pyriprole, sulfluramid, tetradifon, tetrasul, triarathene, verbutin,

furthermore the compound 3-methylphenyl propylcarbamate (Tsumacide Z), the compound 3-(5-chloro-3-pyridinyl)-8-(2,2,2-trifluoroethyl)-8-azabicyclo[3.2.1]octane-3-carbonitrile (CAS Reg. No. 185982-80-3) and the corresponding 3-endo-isomer (CAS Reg. No. 185984-60-5) (cf. WO 96/37494, WO 98/25923), and preparations which comprise insecticidally active plant extracts, nematodes, fungi or viruses.

A mixture with other known active compounds, such as herbicides, or with fertilizers and growth regulators, safeners and/or semiochemicals is also possible.

In addition, the compounds of the formula (I) according to the invention also have very good antimycotic activity. They have a very broad antimycotic activity spectrum in particular against dermatophytes and yeasts, molds and diphasic fungi (for example against Candida species such as Candida albicans, Candida glabrata) and Epidermophyton floccosum, Aspergillus species such as Aspergillus niger and Aspergillus fumigatus, Trichophyton species such as Trichophyton mentagrophytes, Microsporon species such as Microsporon canis and audouinii. The list of these fungi does by no means limit the mycotic spectrum which can be covered, but is only for illustration.

The active compounds can be used as such, in the form of their formulations or the use forms prepared therefrom, such as ready-to-use solutions, suspensions, wettable powders, pastes, soluble powders, dusts and granules. Application is carried out in a customary manner, for example by watering, spraying, atomizing, broadcasting, dusting, foaming, spreading, etc. It is furthermore possible to apply the active compounds by the ultra-low volume method, or to inject the active compound preparation or the active compound itself into the soil. It is also possible to treat the seeds of the plants.

When using the active compounds according to the invention as fungicides, the application rates can be varied within a relatively wide range, depending on the kind of application. For the treatment of parts of plants, the active compound application rates are generally between 0.1 and 10 000 g/ha, preferably between 10 and 1000 g/ha. For seed dressing, the active compound application rates are generally between 0.001 and 50 g per kilogram of seed, preferably between 0.01 and 10 g per

kilogram of seed. For the treatment of the soil, the active compound application rates are generally between 0.1 and 10 000 g/ha, preferably between 1 and 5000 g/ha.

As already mentioned above, it is possible to treat all plants and their parts according to the invention. In a preferred embodiment, wild plant species and plant cultivars, or those obtained by conventional biological breeding, such as crossing or protoplast fusion, and parts thereof, are treated. In a further preferred embodiment, transgenic plants and plant cultivars obtained by genetic engineering, if appropriate in combination with conventional methods (Genetically Modified Organisms), and parts thereof, are treated. The term "parts" or "parts of plants" or "plant parts" has been explained above.

Particularly preferably, plants of the plant cultivars which are in each case commercially available or in use are treated according to the invention. Plant cultivars are to be understood as meaning plants having new properties ("traits") and which have been obtained by conventional breeding, by mutagenesis or by recombinant DNA techniques. They can be cultivars, varieties, bio- or genotypes.

Depending on the plant species or plant cultivars, their location and growth conditions (soils, climate, vegetation period, diet), the treatment according to the invention may also result in superadditive ("synergistic") effects. Thus, for example, reduced application rates and/or a widening of the activity spectrum and/or an increase in the activity of the substances and compositions which can be used according to the invention, better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, better quality and/or a higher nutritional value of the harvested products, better storage stability and/or processability of the harvested products are possible which exceed the effects which were actually to be expected.

The transgenic plants or plant cultivars (i.e. those obtained by genetic engineering) which are preferably to be treated according to the invention include all plants which, in the genetic modification, received genetic material which imparted particularly advantageous useful properties ("traits") to these plants. Examples of such properties are better plant growth, increased tolerance to high or low temperatures, increased tolerance to drought or to water or soil salt content, increased flowering performance, easier harvesting, accelerated maturation, higher harvest yields, better quality and/or a higher nutritional value of the harvested products, better storage stability and/or processability of the harvested products. Further and particularly emphasized examples of such properties are a better defense of the plants against animal and microbial pests, such as against insects, mites, phytopathogenic fungi, bacteria and/or viruses, and also increased tolerance of the plants to certain herbicidally active compounds. Examples of transgenic plants which may be mentioned are the important crop plants, such as cereals (wheat, rice), corn, soybeans, potatoes, cotton, tobacco, oilseed rape and also fruit plants (with the fruits apples, pears, citrus fruits and grapes), and particular emphasis is given to corn, soybeans, potatoes, cotton, tobacco and oilseed

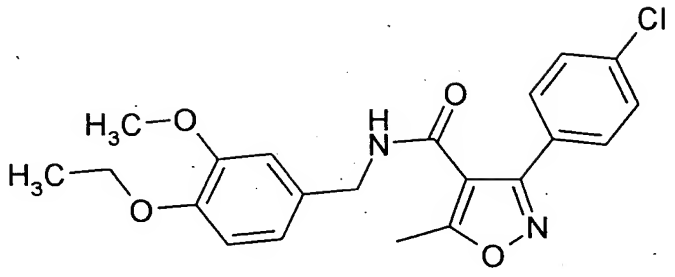
rape. Traits that are particularly emphasized are increased defense of the plants against insects, arachnids, nematodes and slugs and snails by toxins formed in the plants, in particular those formed in the plants by the genetic material from Bacillus thuringiensis (for example by the genes CryIA(a), CryIA(b), CryIA(c), CryIIA, CryIIIA, CryIIIB2, Cry9c, Cry2Ab, Cry3Bb and CryIF and also combinations thereof) (hereinbelow referred to as "Bt plants"). Traits that are also particularly emphasized are the increased defense of the plants against fungi, bacteria and viruses by systemic acquired resistance (SAR), systemin, phytoalexins, elicitors and resistance genes and correspondingly expressed proteins and toxins. Traits that are furthermore particularly emphasized are the increased tolerance of the plants to certain herbicidally active compounds, for example imidazolinones, sulfonylureas, glyphosate or phosphinotricin (for example the "PAT" gene). The genes which impart the desired traits in question can also be present in combination with one another in the transgenic plants. Examples of "Bt plants" which may be mentioned are corn varieties, cotton varieties, soybean varieties and potato varieties which are sold under the trade names YIELD GARD® (for example corn, cotton, soybeans), KnockOut® (for example corn), StarLink® (for example corn), Bollgard® (cotton), Nucoton® (cotton) and NewLeaf® (potato). Examples of herbicide-tolerant plants which may be mentioned are corn varieties, cotton varieties and soybean varieties which are sold under the trade names Roundup Ready® (tolerance to glyphosate, for example corn, cotton, soybean), Liberty Link® (tolerance to phosphinotricin, for example oilseed rape), IMI® (tolerance to imidazolinones) and STS® (tolerance to sulfonylureas, for example corn). Herbicide-resistant plants (plants bred in a conventional manner for herbicide tolerance) which may be mentioned also include the varieties sold under the name Clearfield® (for example corn). Of course, these statements also apply to plant cultivars which have these genetic traits or genetic traits still to be developed, and which will be developed and/or marketed in the future.

The plants listed can be treated according to the invention in a particularly advantageous manner with the compounds of the general formula (I) or the active compound mixtures according to the invention. The preferred ranges stated above for the active compounds or mixtures also apply to the treatment of these plants. Particular emphasis is given to the treatment of plants with the compounds or mixtures specifically mentioned in the present text.

The preparation and the use of the active compounds according to the invention is illustrated in the examples below.

**Preparation Examples**

Example 1

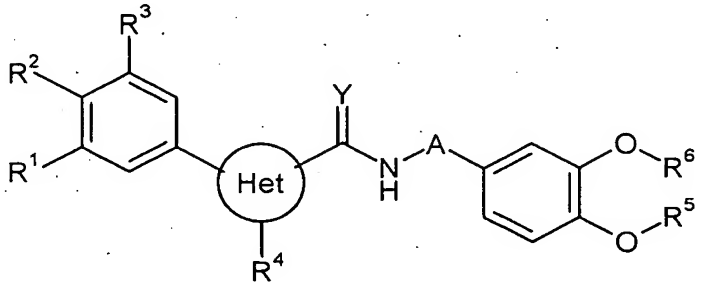


Process a)

At room temperature, 1.285 g (5.061 mmol) of 3-(4-chlorophenyl)-5-methyl-4-isoxazolecarbonyl chloride are added to a solution of 1.201 g (5.518 mmol) of 4-ethoxy-3-methoxybenzylamine hydrochloride in 20 ml of dichloroethane and 1.117 g (11.035 mmol) of triethylamine, and the mixture is stirred under reflux for 1 hour. The mixture is cooled to room temperature, 100 ml of ice-water are added, the mixture is acidified with concentrated hydrochloric acid, dichloroethane is added and the organic phase is separated off, washed with water, dried over sodium sulfate and concentrated under reduced pressure. The residue is recrystallized from isopropanol. This gives 1.1 g (55% of theory) of N4-(4-ethoxy-3-methoxybenzyl)-3-(4-chlorophenyl)-5-methylisoxazole-4-carboxamide of melting point 158°C.

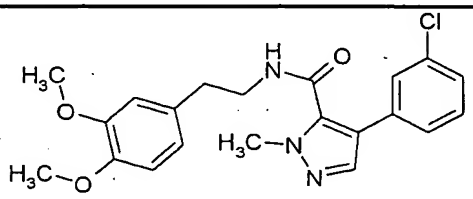
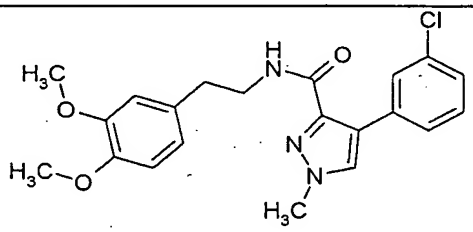
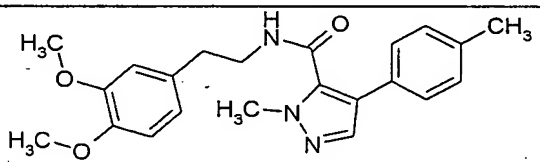
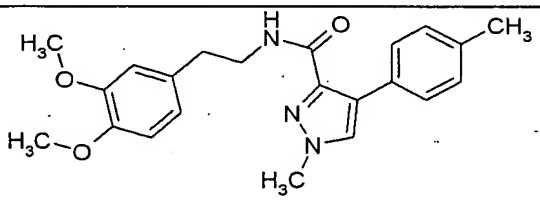
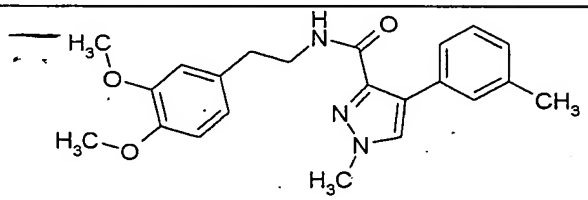
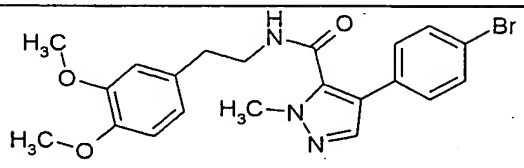
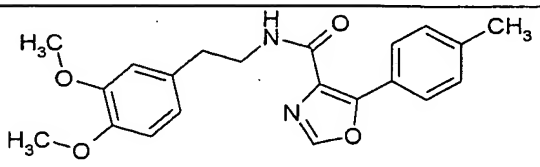
HPLC: LogP = 2.93

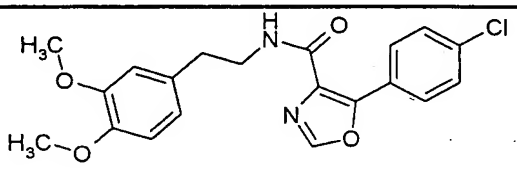
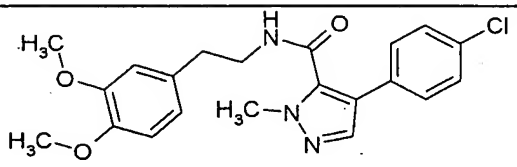
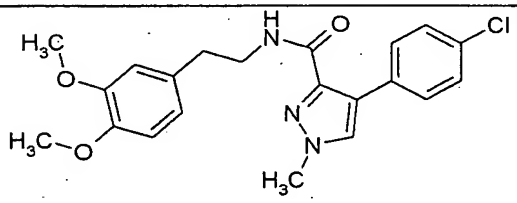
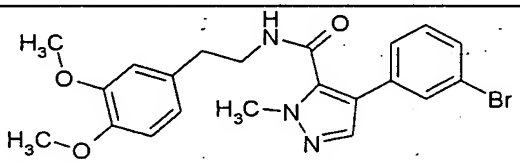
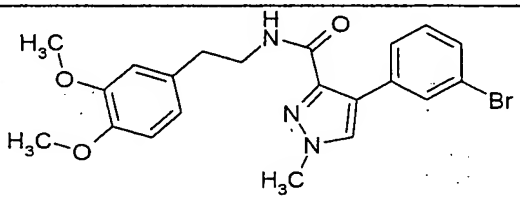
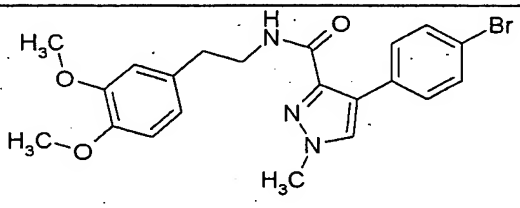
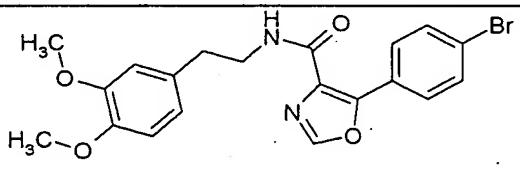
Analogously to Example 1, and in accordance with the general description of the preparation processes a) and b) according to the invention, it is also possible to prepare the compounds of the formula (I) listed in Table 1 below:

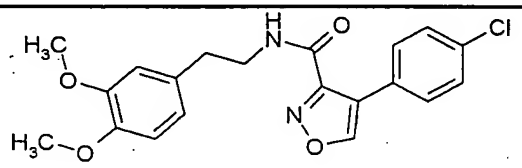
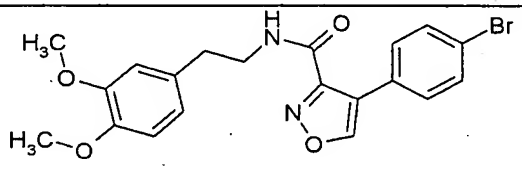
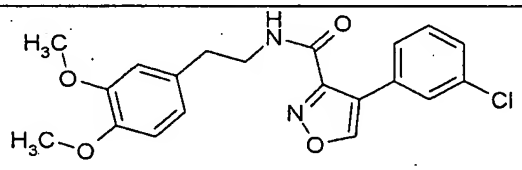
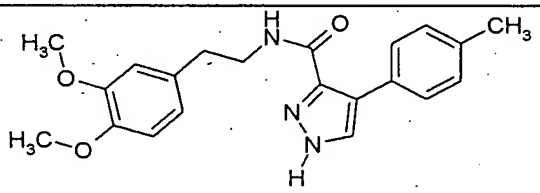
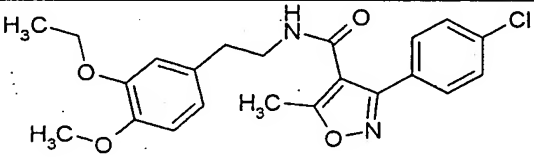
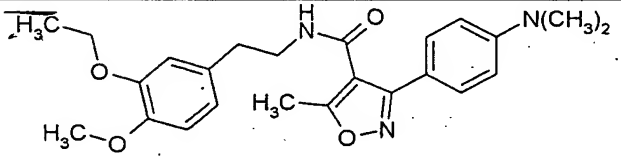
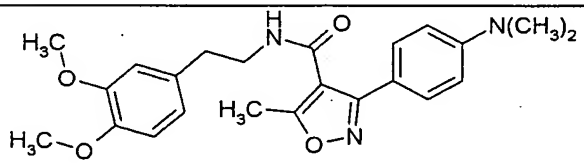
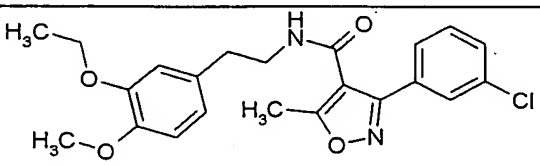


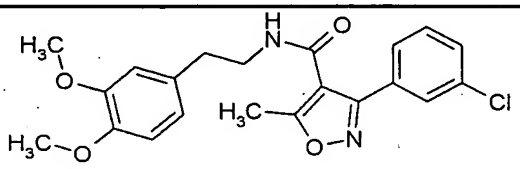
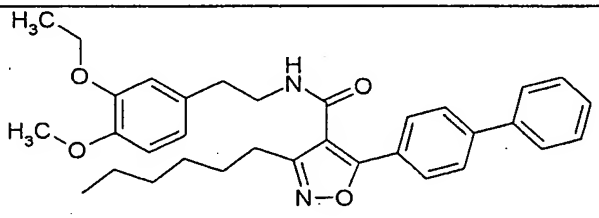
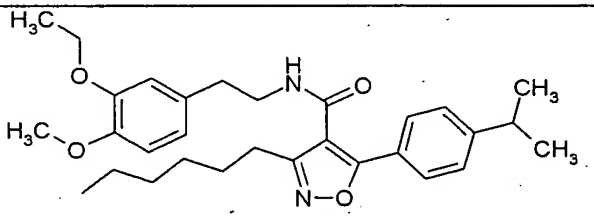
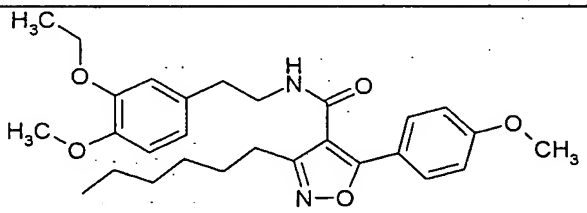
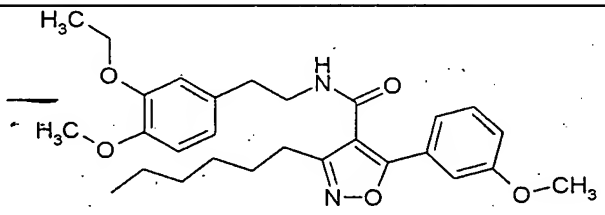
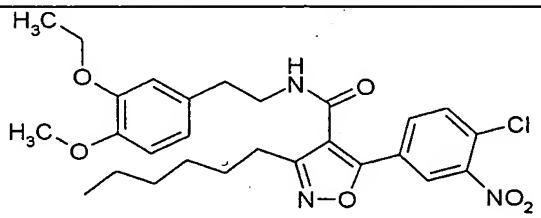
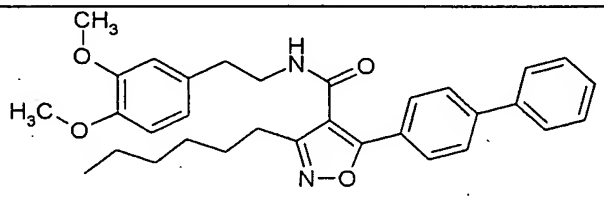
(I)

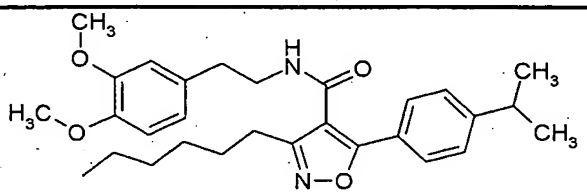
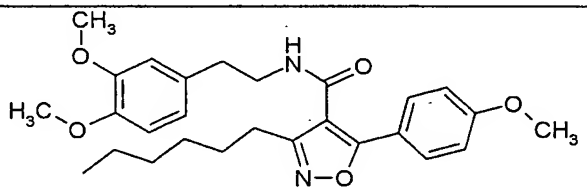
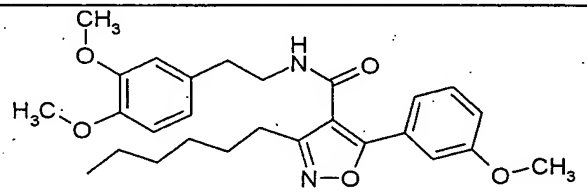
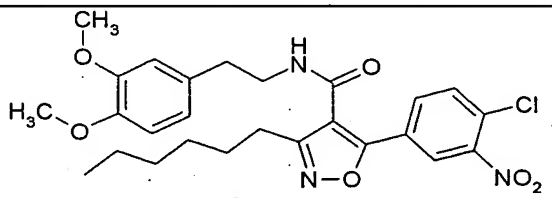
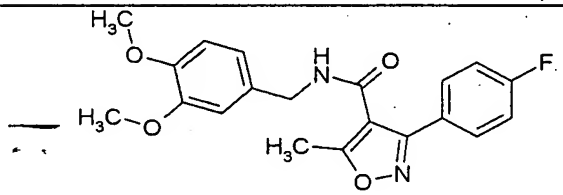
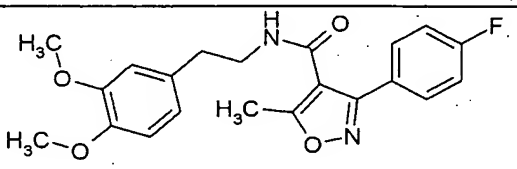
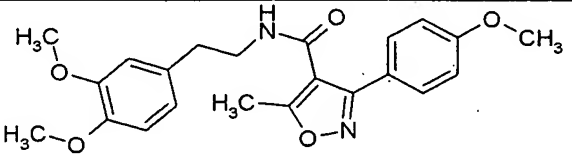
**Table 1**

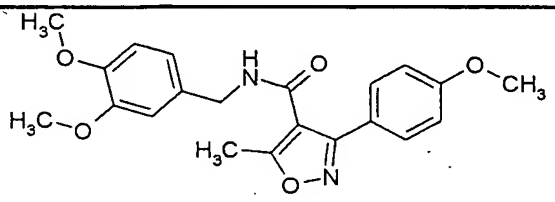
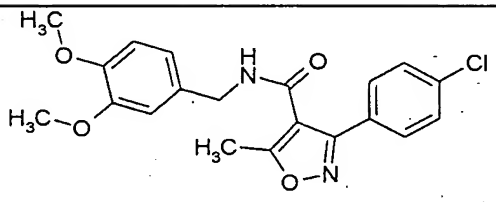
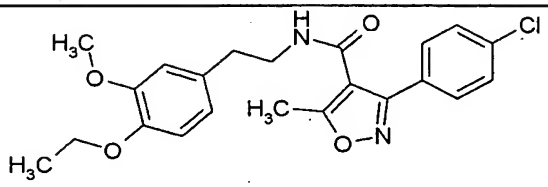
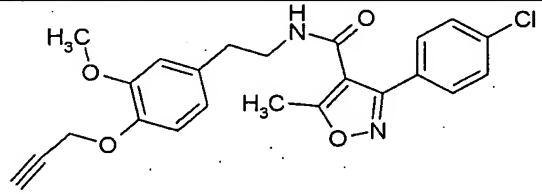
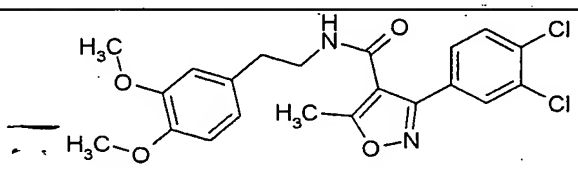
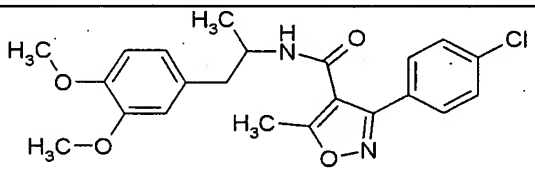
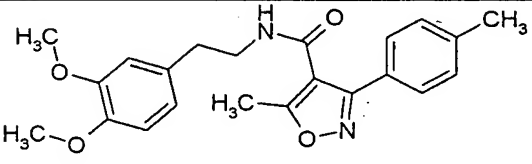
| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 2 |  | 2.60 | |
| 3 |  | 2.78 | |
| 4 |  | 2.52 | |
| 5 |  | 2.60 | |
| 6 |  | 2.58 | |
| 7 |  | 2.68 | |
| 8 |  | | |

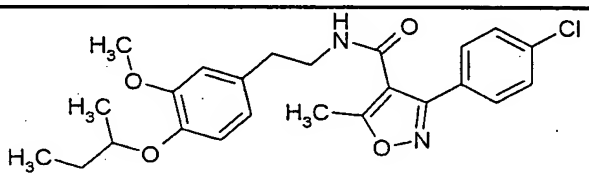
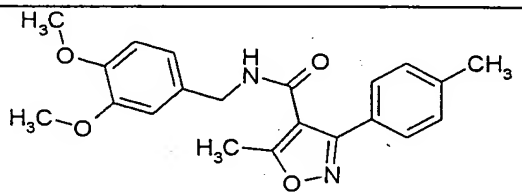
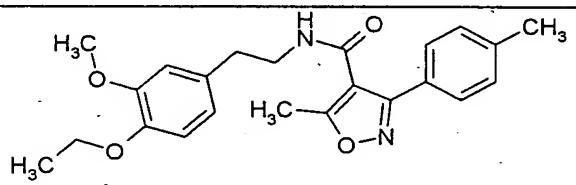
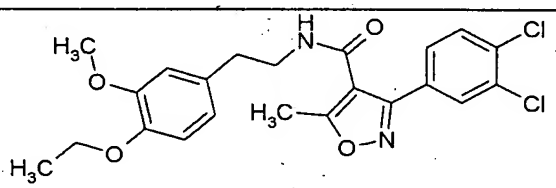
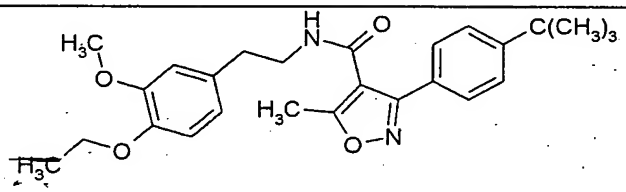
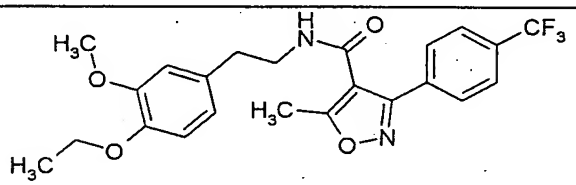
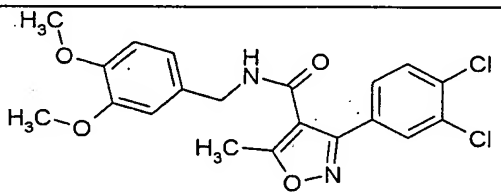
| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 9 |  | 3.28 | |
| 10 |  | 2.60 | |
| 11 |  | 2.77 | |
| 12 |  | 2.69 | |
| 13 |  | 2.87 | |
| 14 |  | 2.87 | |
| 15 |  | 3.40 | |

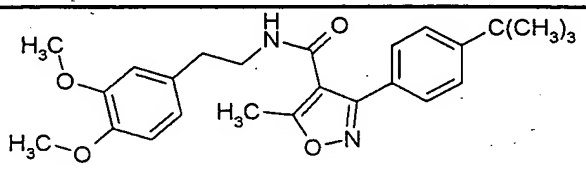
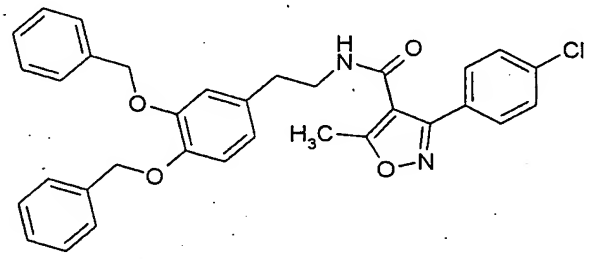
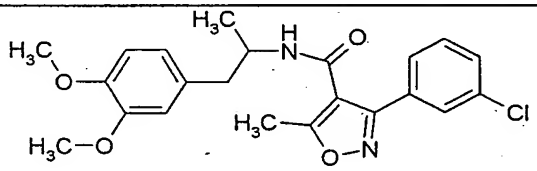
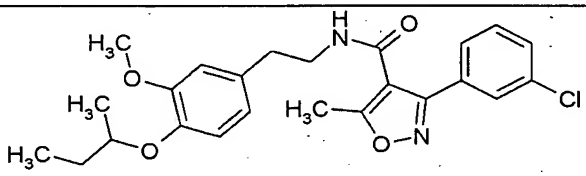
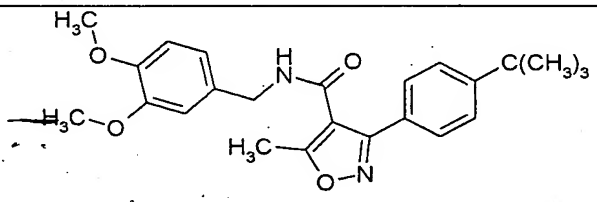
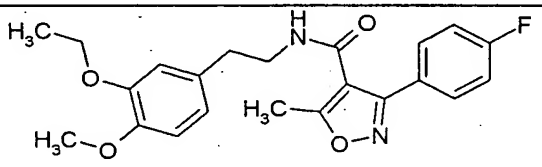
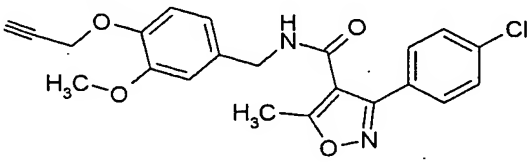
| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 16 |  | 2.93 | |
| 17 |  | | |
| 18 |  | | |
| 19 |  | | |
| 20 |  | 3.04 | |
| 21 |  | | |
| 22 |  | | |
| 23 |  | | |

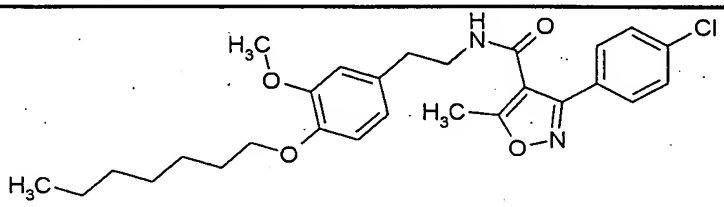
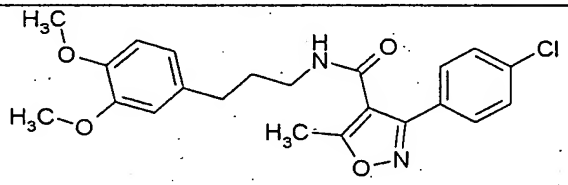
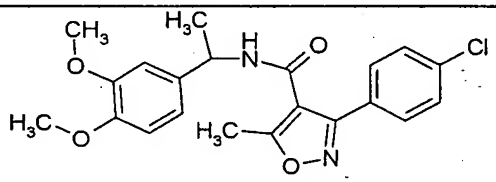
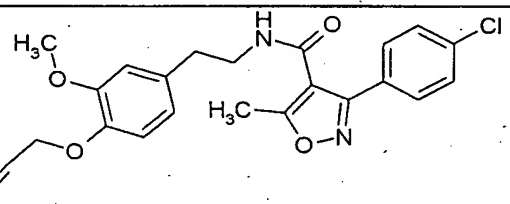
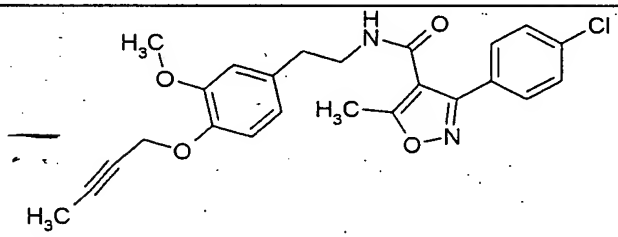
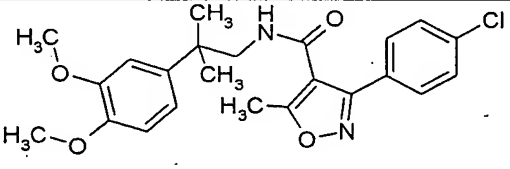
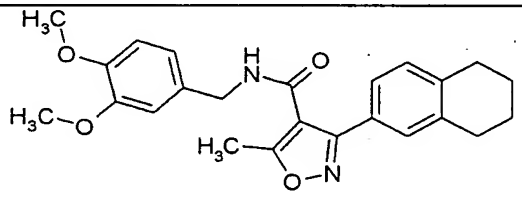
| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 24 |  | | |
| 25 |  | | |
| 26 |  | | |
| 27 |  | | |
| 28 |  | | |
| 29 |  | | |
| 30 |  | | |

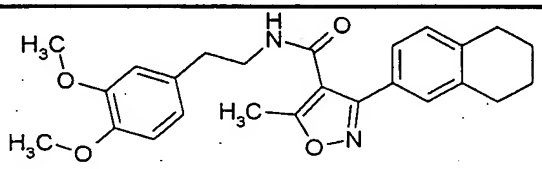
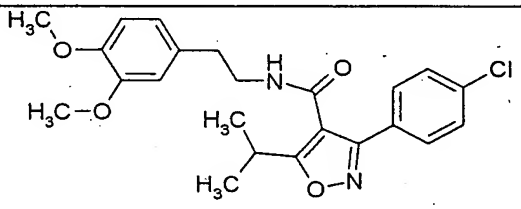
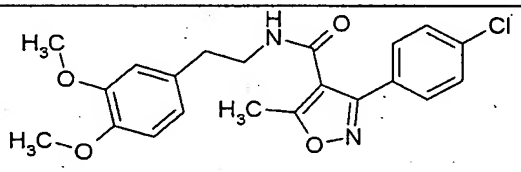
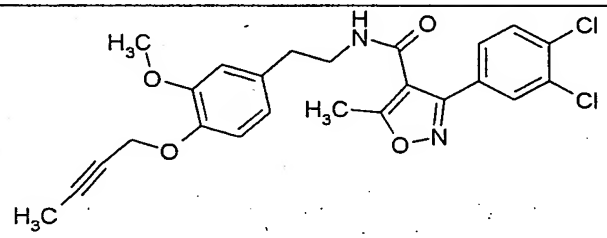
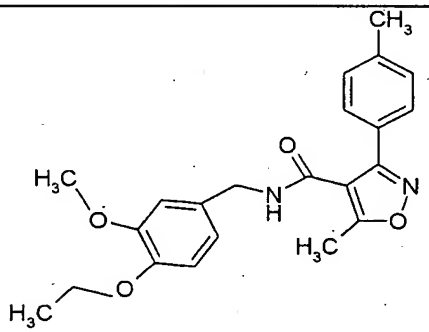
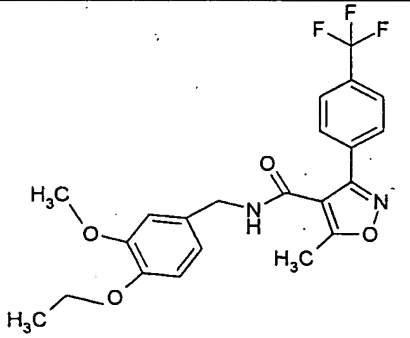
| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 31 |  | | |
| 32 |  | | |
| 33 |  | | |
| 34 |  | | |
| 35 |  | 2.28 | |
| 36 |  | 2.42 | |
| 37 |  | 2.32 | |

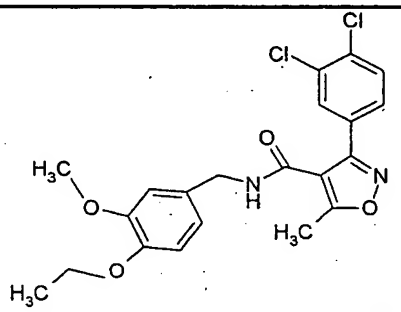
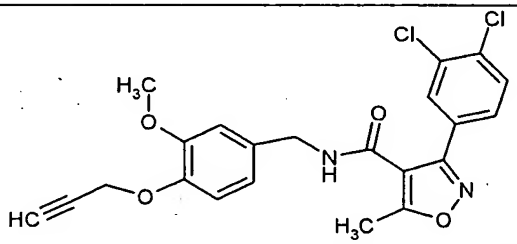
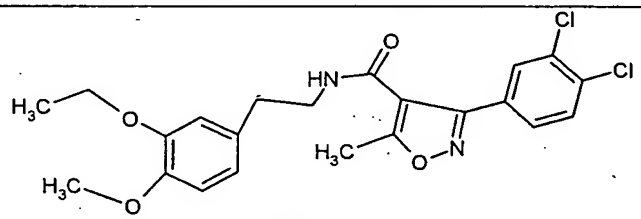
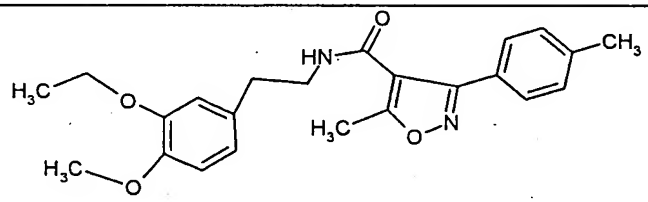
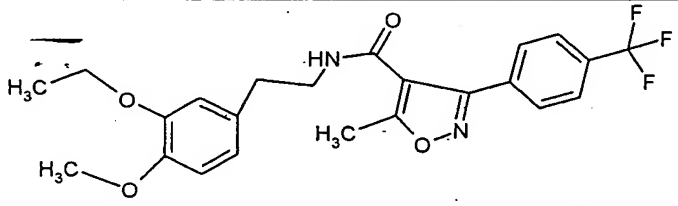
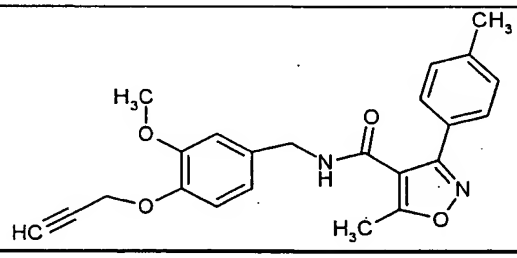
| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 38 |  | 2.18 | |
| 39 |  | 2.59 | |
| 40 |  | 3.07 | |
| 41 |  | 2.96 | 128 |
| 42 |  | 3.16 | |
| 43 |  | 2.91 | |
| 44 |  | 2.58 | |

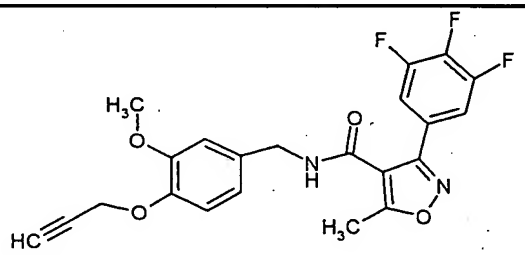
| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 45 |  | 3.78 | |
| 46 |  | 2.51 | |
| 47 |  | 3.00 | |
| 48 |  | 3.63 | |
| 49 |  | 3.85 | |
| 50 |  | 3.41 | |
| 51 |  | 3.09 | |

| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 52 |  | 3.42 | |
| 53 |  | 4.66 | |
| 54 |  | 2.99 | |
| 55 |  | 3.85 | |
| 56 |  | 3.33 | |
| 57 |  | 2.72 | |
| 58 |  | 2.83 | 133 |

| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 59 |  | 5.16 | |
| 60 |  | 2.95 | |
| 61 |  | 2.76 | 180 |
| 62 |  | 3.26 | 119 |
| 63 |  | 3.25 | |
| 64 |  | 3.93 | |
| 65 |  | 3.07 | |

| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 66 |  | 3.27 | |
| 67 |  | 3.30 | |
| 68 |  | 2.74 | |
| 69 |  | 3.70 | |
| 70 |  | 2.78 | |
| 71 |  | 3.19 | |

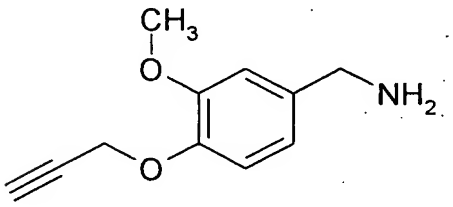
| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 72 |  | 3.35 | |
| 73 |  | 3.26 | |
| 74 |  | 3.53 | |
| 75 |  | 2.9 | |
| 76 |  | 3.3 | |
| 77 |  | | |

| Ex. No | Structure | logP | m.p. (°C) |
|---|---|---|---|
| 78 |  | 3.09 | |

The logP values were determined in accordance with EEC Directive 79/831 Annex V. A[8] by HPLC (gradient method, acetonitrile/0.1% aqueous phosphoric acid)

**Preparation of the precursors of the formula (III)**

Example (III-a-1)



Process c)

To a solution of 4.1 g (21.620 mmol) of 4-hydroxy-3-methoxybenzylamine hydrochloride in 50 ml of ethyl acetate and 5 ml of triethylamine are added 4.954 g (22.7 mmol) of di-tert-butyl pyrocarbonate, and the mixture obtained is stirred at room temperature for 18 hours. Then, 100 ml of ethyl acetate are added, the mixture is washed with 50 ml of water and then with 50 ml of dilute citric acid and 50 ml of sodium bicarbonate solution and finally with 50 ml of saturated sodium chloride solution. The organic phase is dried over sodium sulfate and concentrated under reduced pressure.

This gives 3.7 g (67% of theory) of tert-butyl 4-hydroxy-3-methoxybenzylcarbamate (VI-a*-1)

HPLC: logP = 1.91

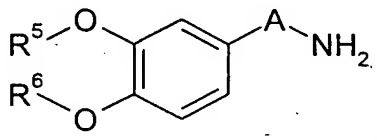
To a solution of 3.7 g (14.607 mmol) of tert-butyl 4-hydroxy-3-methoxybenzylcarbamate (VI-a*-1) in 50 ml of acetone are added 5.43 g (36.519 mmol) of propargyl bromide, 5 g of anhydrous potassium carbonate and 0.15 g of potassium iodide, and the mixture obtained is heated under reflux for 18 hours. The reaction mixture is added to 100 ml of water and extracted with 200 ml of ether. The organic phase is washed twice with 10% strength aqueous sodium hydroxide solution, dried over sodium sulfate and concentrated. This gives 3.2 g (73% of theory) of tert-butyl 4-(propargyloxy)-3-methoxybenzylcarbamate (III-a*-1).

(HPLC: logP = 2.57).

To a solution of 3.2 g (10.984 mmol) of tert-butyl 4-(propargyloxy)-3-methoxybenzylcarbamate in 50 ml of ethyl acetate are added 3 ml of a concentrated hydrogen chloride solution, the mixture obtained is stirred at room temperature for 18 hours and the resulting precipitate is filtered off. The precipitate is washed twice with ethyl acetate and dried under reduced pressure. This gives 2.0 g (79% of theory) of 4-(propargyloxy)-3-methoxybenzylamine hydrochloride (III-a-1)

(HPLC: logP = 0.20).

Analogously, and in accordance with the general description of the preparation process c) according to the invention, it is also possible to prepare the compounds of the formula (III) listed in Table 2 below:



(III)

**Table 2**

| Ex. No | $R^5$ | $R^6$ | A | logP |
|---|---|---|---|---|
| III-a-2 | $CH_3$ | 2-butynyl | $(CH_2)_2$ | 0.80 |
| III-a-3 | $CH_3$ | allyl | $CH_2$ | |
| III-a-6 | $CH_3$ | $CH_2$-CN | $CH_2$ | |
| III-b-1 | allyl | $CH_3$ | $CH_2$ | |
| III-b-2 | $CH_2$-CN | $CH_3$ | $CH_2$ | |
| III-b-3 | propargyl | $CH_3$ | $(CH_2)_2$ | |

The logP values were determined in accordance with EEC Directive 79/831 Annex V. $A^8$ by HPLC (gradient method, acetonitrile/0.1% aqueous phosphoric acid)

**Use examples:**

Example A

Phytophthora test (tomato)/protective

| | |
|---|---|
| Solvents : | 24.5 parts by weight of acetone |
| | 24.5 parts by weight of dimethylacetamide |
| Emulsifier : | 1 part by weight of alkylaryl polyglycol ether |

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvents and emulsifier, and the concentrate is diluted with water to the desired concentration.

To test for protective activity, young plants are sprayed with the preparation of active compound at the stated application rate. After the spray coating has dried on, the plants are inoculated with an aqueous spore suspension of Phytophthora infestans. The plants are then placed in an incubation cabin at about 20°C and 100% relative atmospheric humidity.

Evaluation is carried out 3 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

In this test, the compounds according to the invention listed in Examples 1, 24, 38, 39, 40, 41, 42, 46, 47, 48, 50, 51, 54, 58, 61, 6 and 68 exhibit, at an application rate of 100 g/ha, an efficacy of 94% or more.

Example B

Plasmopara test (grapevine)/protective

Solvents : 24.5 parts by weight of acetone
24.5 parts by weight of dimethylacetamide

Emulsifier : 1 part by weight of alkylaryl polyglycol ether

To produce a suitable preparation of active compound, 1 part by weight of active compound is mixed with the stated amounts of solvents and emulsifier, and the concentrate is diluted with water to the desired concentration.

To test for protective activity, young plants are sprayed with the preparation of active compound at the stated application rate. After the spray coating has dried on, the plants are inoculated with an aqueous spore suspension of Plasmopara viticola and then remain in an incubation cabin at about 20°C and 100% relative atmospheric humidity for 1 day. The plants are then placed in a greenhouse at about 21°C and about 90% atmospheric humidity for 4 days. The plants are then moistened and placed in an incubation cabin for 1 day.

Evaluation is carried out 6 days after the inoculation. 0% means an efficacy which corresponds to that of the control, whereas an efficacy of 100% means that no infection is observed.

In this test, the compounds according to the invention listed in Examples 1, 24, 35, 36, 38, 39, 40, 41, 42, 43, 44, 46, 47, 48, 49, 50, 51, 54, 56, 58, 61, 62 and 68 exhibit, at an application rate of 100 g/ha, an efficacy of 90 % or more.